Published in "Physical Chemistry Chemical Physics 11(): 10175-10179, 2009"
which should be cited to refer to this work.

Reversible formation of gold nanoparticle–surfactant composite assemblies for the preparation of concentrated colloidal solutions

Natallia Shalkevich,[a] Andrey Shalkevich,[b] Lynda Si-Ahmed[c] and Thomas Bürgi*[ad]

We have developed a simple method for the preparation of nearly mono-dispersed stable gold colloids with a fairly high concentration using a two step procedure. First we synthesize citrate capped gold nanoparticles and then exchange the citrate ions with triethyleneglycolmono-11-mercaptoundecylether (EGMUDE). This leads to the immediate precipitation and formation of composite assemblies. The gold nanoparticles were successfully self-redispersed after a few days. The prepared gold colloid can be easily concentrated up to 20 times by separation of the flocculated part. UV-visible spectra, transmission electron microscopy (TEM), and dynamic light scattering (DLS) were used to characterize the products thus formed.

Introduction

During the past years, the synthesis and characterization of nanoparticles has become a focus of both fundamental science and technical applications because of their unique characteristics such as catalytic activity, optical, electronic, thermal, magnetic[1] and other properties.[2] In particular, gold nanoparticles are currently being explored for example in catalysis,[3] chemical sensing,[4,5] molecular labeling,[6] gene delivery,[7] and photonics.[7]

There are many established methods for gold colloid syntheses, such as conventional chemical reduction,[8] heat-treatment,[9] microwave irradiation,[10,11] sonochemical,[12] photolytical[13] and seeding growth approach,[14] to mention a few. Most of these methods utilize thiols as capping agents in order to improve nanoparticle stability. Thiolated modifiers provide enhanced stabilization through the sterical interaction between surface layers and/or their charge repulsion. Nevertheless only relatively dilute colloids can be obtained by direct reduction because concentrated solutions result in the formation of a precipitate. Another problem arises from the fact that larger gold nanoparticles (above 15–20 nm) require significantly stronger stabilization to prevent agglomeration.

In this paper, we report the facile synthesis of gold nanoparticles by using the Turkevich–Frens[15] method with further ligand exchange. We have made the discovery that triethyleneglycolmono-11-mercaptoundecylether (EGMUDE) in the presence of citrate capped gold in an aqueous medium is able not only to yield highly stable nanoparticles but also segregate them into a concentrated phase. In contrast to previous syntheses where the prepared colloid needs to be additionally concentrated, the current synthesis provides suspensions of highly stable gold nanoparticles at high concentration.

[a] *Université de Neuchâtel, Institut de Physique, Laboratoire de chimie physique des surfaces, Rue Emile-Argand 11, 2009 Neuchâtel, Switzerland*
[b] *University of Fribourg, Adolphe Merkle Institute and Fribourg Center for Nanomaterials, Route de l'ancienne Papeterie CP 209, CH-1723 Marly, Switzerland*
[c] *Metalor Technologies SA, Av. du Vignoble, Case postale 9, 2009 Neuchâtel 9, Switzerland*
[d] *Ruprecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany. E-mail: buergi@uni-heidelberg.de*

Experimental section

Materials

Hydrogen tetrachloroaurate(III) solution was supplied by Metalor Technologies SA, Neuchâtel, Switzerland. Trisodiumcitrate dihydrate and triethyleneglycolmono-11-mercaptoundecylether (95%) (EGMUDE) were purchased from Sigma-Aldrich. Ethanol (99.9%) was purchased from Merck. All reagents were used as received. Milli-Q (Millipore) water with a resistivity of 18.2 MΩ was employed throughout. Dialysis membranes (3.5 kDa, Spectra/Por CE) were obtained from Spectrum.

Instrumentation

UV-visible spectra (200–900 nm) were recorded on a Cary 300 spectrometer using a quartz cell of 1 cm path length. Transmission electron micrographs (TEM) were obtained with a Philips C 200 microscope in bright field mode at a voltage of 200 kV. The samples for TEM study were prepared by casting a few drops of the gold colloid onto carbon-coated copper grids (300 mesh) and used after solvent evaporation in air.

Dynamic light scattering (DLS) was performed with an ALV-5000 spectrophotometer equipped with an argon-laser (Coherent, model Innova 300, $\lambda = 488$ nm), a digital auto-correlator (ALV) and a variable angle detection system. Measurements were made at a fixed scattering angle of 90° and a temperature of 25.0 ± 0.1 °C. The individual correlation functions were analyzed using a second-order cumulant fit.

Synthesis of gold nanoparticles

17 nm gold nanoparticles were prepared by the classical method described by Turkevich and Frens.[15,16] 50 ml of Milli-Q water slightly stirring were heated to 90 °C in a

flat-bottomed flask closed by a cover-glass. 6.5 μl of hydrogen tetrachloroaurate(III) solution (0.028 mmol) were quickly added into hot water and then heated to 97–98 °C. 24.9 mg of sodium citrate (0.084 mmol) were dissolved in 1.25 ml of Milli-Q water and rapidly introduced into the boiling gold solution. A color change from pale yellow through colorless to red took place in 15 s. The mixture was kept boiling for 15 min and then cooled to room temperature.

Preparation of EGMUDE-modified gold nanoparticles

Gold colloid was purified *via* dialysis before ligand addition. For this, 50 ml of gold–citrate colloid were transferred to a 3.5 kDa membrane and dialyzed against Milli-Q water in a 2 l beaker. The water was changed every 10 h over the course of a week. After dialysis not more than 10% of the gold was lost, as was determined by UV-visible spectroscopy from the absorption of the plasmon band.

Functionalization of the gold nanoparticles with EGMUDE was accomplished by ligand addition to dialyzed citrate stabilized gold colloid in a 1 : 2.5 molar ratio of Au atoms to thiol molecules. EGMUDE was added as a colloidal solution (micellar solution), which was prepared in the following way: 0.07 mmol of thiol were added to 5 ml of Milli-Q water and stirred for 2 min. The emulsion was injected into 50 ml of well-stirred gold colloid (initial gold concentration of 0.55 mM was diminished to 0.5 mM after dialysis). The color of the mixture quickly turned to black, the particles seemed to agglomerate. Without the stirring the particles were precipitated at the bottom of the flask. After one day, on shaking the slightly colored sediment, the particles were back into solution indicating that the agglomeration process was reversible. After 5 days, the particles were completely redispersed without any need to stir them.

The water was rotary evaporated and EGMUDE-modified gold particles were washed with a small quantity of ethanol to remove the excess thiol. This purification method relies on the fact that the free thiol is soluble in ethanol, whereas the particles are hardly soluble. The gold nanoparticles were redispersed in a small volume of water, up to a concentration of 1 vol%. Under these conditions the particles could be kept at least for several months without noticeable change.

Use of the gold colloid without dialysis for the modification with EGMUDE was not successful. In fact, the thiol exchange took place but no formation of supramolecular agglomerates was observed. The effect of the dialysis is a reduction of the ionic strength (citrate and sodium ions), which leads to an increase of the width of the electrical double layer. The gold–EGMUDE nanoparticles formed without the dialysis (in the absence of supramolecular assemblies) were less stable than the ones formed within the assemblies, *i.e.* with the dialyzed sample, which indicates incomplete ligand exchange. In fact, during the cleaning with ethanol a part of the particles prepared with the undialyzed gold colloid showed irreversible agglomeration, whereas the sample prepared within the supramolecular assemblies was perfectly stable.

Results and discussion

Citrate stabilized gold colloid

The thermal citrate reduction of gold(III) in a 1 : 3 Au : citrate molar ratio produced homogeneous spherical particles with a diameter of *ca.* 17 nm (Fig. 1a). The particles exhibited one narrow absorbance band at 523 nm in the UV-visible spectra which is attributed to the surface plasmon resonance (SPR) band of monodisperse and well-separated gold nanoparticles (Fig. 2a). The dialysis of citrate stabilized gold colloid was performed to eliminate the byproducts, such as sodium ions, excess citrate and its oxidation product.

The purified gold colloid (Fig. 3a) displayed UV-visible spectra with a maximum at 524 nm. No signals were observed in the UV-region that could be attributed to byproducts (excess citrate and its oxidation products). This shows that the latter were successfully removed from the sample during the dialysis (Fig. 2a). The small broadening of the SPR band can be related to slight agglomeration of gold nanoparticles.

Gold surface modification *via* triethyleneglycolmono-11-mercaptoundecylether (EGMUDE)

Modification of the gold surface with EGMUDE was carried out by the addition of thiol (EGMUDE) into dialyzed gold colloid in a 1 : 2.5 Au : thiol molar ratio. EGMUDE was mixed with a small quantity of water forming a turbid solution due to limited solubility of EGMUDE in water. While the EGMUDE was injected, the gold nanoparticles aggregated, which could be easily observed by eye, and rapidly precipitated (Fig. 3b and c). Four minutes later almost no absorption band could be found in UV-visible spectra shown in Fig. 2b. The

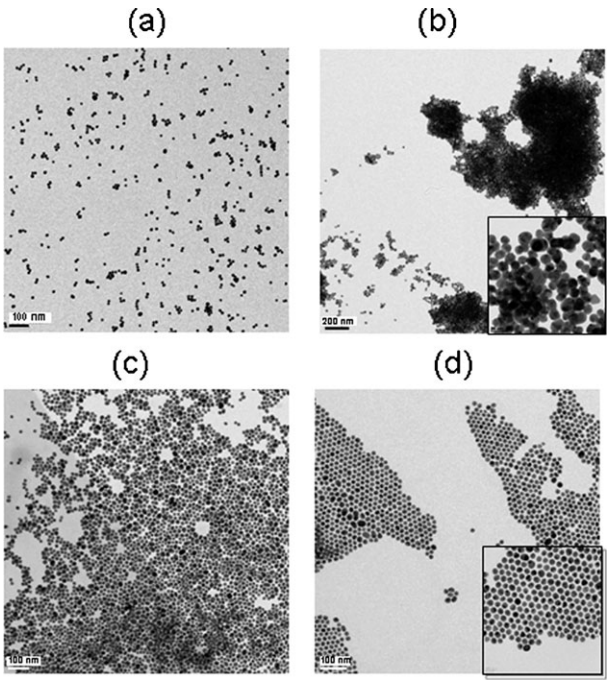

Fig. 1 Transmission electron microscopy graphs of gold nanoparticles with a diameter of *ca.* 17 nm before ligand exchange (a) and after EGMUDE addition at different time intervals: 4 minutes (b), 1 day (c) and 7 days (d). Inset is a magnified part of the corresponding image.

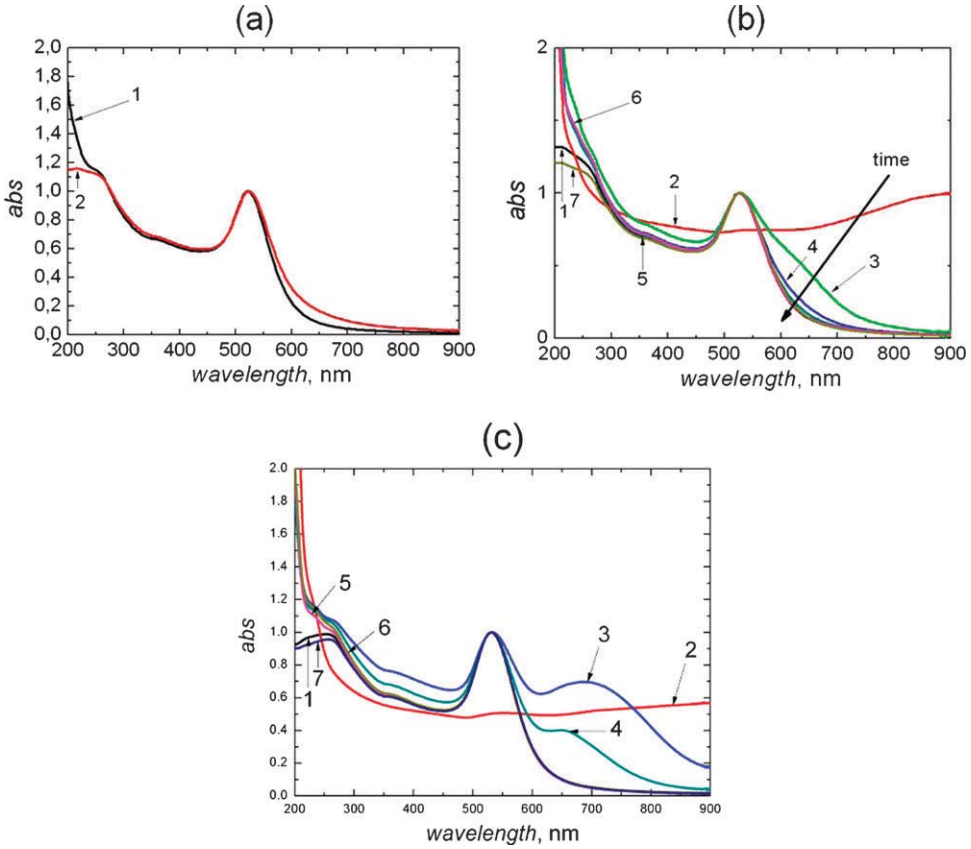

Fig. 2 UV-visible absorption spectra (a) of citrate covered 17 nm gold colloid before (1) and after (2) dialysis, (b) of 17 nm gold colloid before (1) and after EGMUDE addition at different time intervals: after 4 minutes (2), 15 hours (3), 1 day (4), 2 days (5), 7 days (6) and purified with EtOH (7), and (c) of 40 nm gold colloid before (1) and after EGMUDE addition at different time intervals: after 30 minutes (2), 1 day (3), 2 days (4), 3 days (5), 7 days (6) and purified with EtOH (7).

electron micrograph (Fig. 1b) demonstrates as well very compact and dense aggregates without any separation between particles.

The position of the surface plasmon band directly reflects the distance between the metal particles.[17] It has been shown that there is a significant shift of the surface plasmon band at relative distances between the nanoparticles $d/(2R)$ (R is the nanoparticle radius, d is the center-to-center distance) smaller than about 1.4. Therefore, for particles of 17 nm in diameter strong shifts due to the interaction of the plasmons are expected for center-to-center distances smaller than $d = 23.8$ nm ($= 1.4 \times 17$ nm), which corresponds to a separation of the nanoparticle surfaces of 6.8 nm ($= 23.8 - 17$ nm). For comparison, the fully extended EGMUDE molecule has a length of 2.76 nm, as determined by energy minimization using HyperChem. For example, Fig. 2b shows a secondary plasmon band with a shift of about 100 nm after 15 h. According to the work of Schiffrin and co-workers[17] a shift of 100 nm corresponds to a relative distance $d/(2R)$ of less than 1.1 and therefore a distance between the surfaces of adjacent gold nanoparticles of less than 1.7 nm. This is more than the interparticle distance of 2×0.3 nm $= 0.6$ nm caused by adsorbed citrate ions but significantly less than the distance expected for gold nanoparticles fully covered by EGMUDE but touching each other, where a distance of 2×2.76 nm $= 5.52$ nm is expected, assuming no interpenetration of the two stabilizer layers on adjacent nanoparticles. For the latter distance a shift of less than 20 nm would be expected. It should be noted that these values change quantitatively for different particle sizes. Indeed we observed qualitatively the same phenomena for 40 nm particles (Fig. 2c) upon functionalization by EGMUDE, however with correspondingly more pronounced shifts of the secondary plasmon band. This is due to the fact that for the 40 nm particles the relative distances $d/(2R)$ are correspondingly smaller due to the larger particle size.

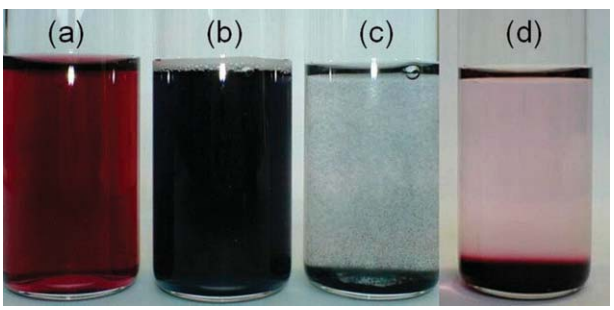

Fig. 3 Vials with different gold colloids: (a) citrate covered, (b) just after EGMUDE addition, (c) after 10 min and (d) after 1 day.

Interestingly, a slightly red-colored layer above the precipitate was noted one day after ligand addition (Fig. 3d). The gold

nanoparticles "self-redispersed" under a gentle shaking and formed a homogeneous colored solution. Analysis of the electron micrograph (Fig. 1c) of the sample one day after EGMUDE addition shows that the gold nanoparticles distribute more homogeneously without any agglomeration. The broadened SPR band appears again (Fig. 2b) however with a small shift of 3 nm to longer wavelength. It is well-known[18,19] that the exact position of the plasmon band is extremely sensitive both to particle size and shape and to the optical and electronic properties of the medium surrounding the particles. The red-shift of the plasmon band can be explained by an increase in the local refractive index of the surrounding medium of gold nanoparticles *i.e.* by adsorbed EGMUDE. The secondary plasmon band becomes less pronounced with time (Fig. 2b, 2 days) and after one week it coincides with the one observed for the initial gold colloid except for the slight red-shift by 3 nm due to the adsorbed EGMUDE (Fig. 2b, 7 days). This observation shows that the citrate layers of gold nanoparticles were replaced by a new EGMUDE protecting layer, which stabilizes the particles and prevents them from aggregation. A TEM micrograph (Fig. 1d) shows the gold nanoparticles a week after EGMUDE was added. The particles are well-separated from each other and they can form ordered structures on the surface of the TEM copper grid under the pinning effect and entropy-driven ordering tendency upon solvent evaporation.[2] No UV-band in the absorption spectra of the gold colloid purified by ethanol is observed that could be attributed to EGMUDE (Fig. 2b) showing that the latter was removed from solution during purification.

In order to directly study the cluster formation and further re-dispersion of gold nanoparticles at different times after ligand addition dynamic light scattering measurements were performed.

Fig. 4 shows the correlation functions for the gold colloids at different stages. Initial citrate capped gold nanoparticles exhibit a correlation curve with the smallest decorrelation time and relatively low polydispersity. Cumulant analysis gives a hydrodynamic radius of the particles of around 10 nm. This is slightly larger than that determined from TEM analysis most likely due to the hydrodynamic layer on the particles. EGMUDE solution was directly added into the cylindrical cell containing gold colloid and was kept in the sample chamber for 10 minutes in order to stabilize the temperature. The correlation curve of this sample showed drastic changes with respect to the initial colloid: the decorrelation time shifted to much higher lag times and the baseline became unstable and deviated from zero. These changes indicate the formation of very large clusters (with hydrodynamic radii larger than 150 nm) usually observed in destabilized suspensions. The sample was afterwards kept in a thermostat for one day and measured again. The correlation curve obtained from this sample exhibited significant shift to the lower lag times due to decreasing cluster size. The same tendency was observed for the samples measured even later: the correlation curves of the system approached the one of the initial colloid. The small discrepancy at low intercept close to the baseline arises from a few small clusters in the system. Therefore it can be concluded that after six days the system does not contain large clusters

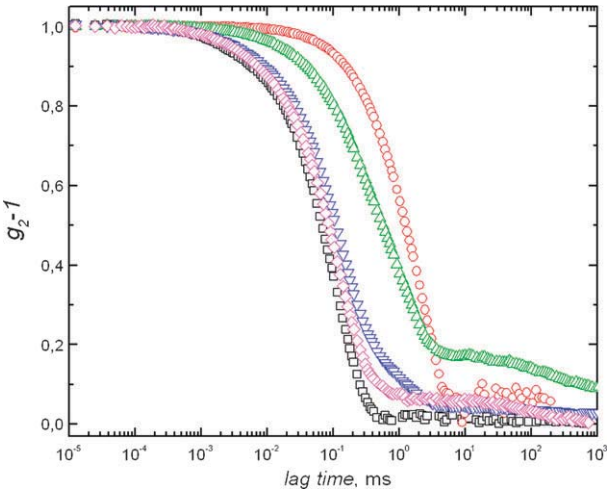

Fig. 4 The normalized electric field autocorrelation functions of gold colloids before ligand exchange (□), just after EGMUDE addition (○), after 1 day (△), 3 (▽) and 6 days (◇).

anymore and only individual EGMUDE coated gold nanoparticles are present. The observed self-re-dispersion of the nanoparticles indicates the remarkably high efficiency of the EGMUDE protection.

We considered the possibility that the clusters of gold nanoparticles are organized within the big micelles or the lamellas formed by the EGMUDE, which consists of hydrophilic (triethyleneglycol chain) and hydrophobic (hydrocarbon C_{11}–chain) blocks and which can be considered as a non-ionic surfactant. Critical micelle concentration (CMC) of EGMUDE is not described in the literature but can be estimated by comparison with a linear ethoxylate surfactant with a similar structure *i.e.* triethyleneglycolundecylether (EGUDE). There are several empirical relationships in the literature[20–23] to predict CMC for linear alkyl ethoxylates. The CMC of EGUDE which is equal to 1.42×10^{-4} mol l^{-1} was calculated using the three-parameter empirical model proposed by Ravey[21]

$$\log_{10}\mathrm{CMC} = 1.904 - 0.524C\# + 0.000442C\# \times \mathrm{EO}\#$$

where $C\#$ is the number of carbon atoms in the hydrocarbon chain and EO# is the number of ethylene oxide groups.

The EGMUDE concentration in the gold colloid was 1.27×10^{-3} mol l^{-1}, which is 9 times higher than the CMC of EGUDE. Under these conditions the surfactant molecules form assemblies, for example micelles, to reduce system energy. The formation of such assemblies is in fact indicated by TEM measurements (Fig. 5). Clearly the EGMUDE–nanoparticle composite shows some hierarchical organization. Within the entire entity with a diameter of about 6 μm domains of about 1 μm are visible with very high local concentration of gold nanoparticles. Similar nanoparticle composite structures have been observed recently when flocculating citrate stabilized gold nanoparticles with a polycation.[24] However, in contrast to our case, the changes observed, for example in the UV-visible spectra, were not reversible. Note that the preparation method of gold

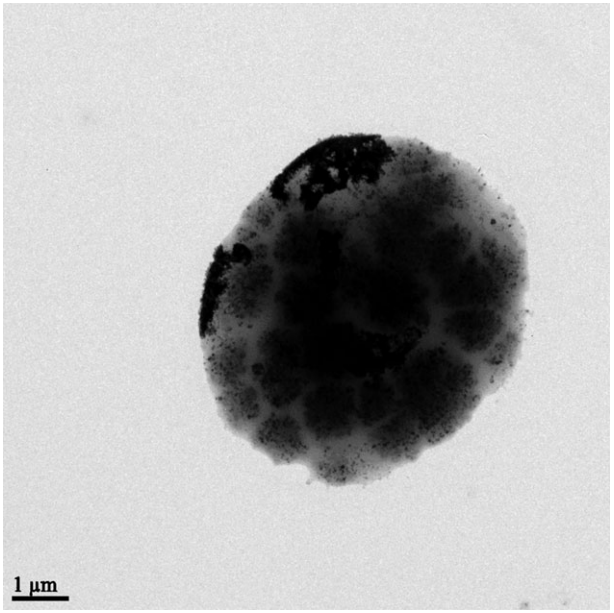

Fig. 5 Transmission electron microscopy graph of the assemblies of EGMUDE and gold nanoparticles, 10 min after ligand addition.

nanoparticles presented here relies on the fact that the thiol (EGMUDE) forms micelles in water.

The ligand exchange on the gold nanoparticle surface takes place within these structures and therefore at locally extremely high EGMUDE concentrations. The ligand exchange process is a critical point with respect to nanoparticle stability. The gold nanoparticles are initially charge stabilized due to the adsorbed citrate. Once the particles are fully covered by EGMUDE they are sterically stabilized. During the exchange there is however a critical point where the charge diminishes but the sterical stabilization is not yet fully established. To avoid agglomeration at this point the exchange is normally done in dilute solutions in order to minimize particle collisions during the critical phase. In contrast, the results presented above show that in our system the exchange is taking place within supramolecular assemblies where the nanoparticle concentration is locally extremely high. This is a strong indication that within these assemblies the EGMUDE leads to an organization of the nanoparticles that prevents them from irreversible agglomeration. The surface functionalization goes hand in hand with a structural change within the composite assemblies. This is clearly indicated by the changes in the UV-visible spectra. The position of the shifted plasmon band shows that at the beginning of the process the distance between fractions of the gold nanoparticles is very small, in agreement with TEM. This distance then increases with time until the particles are fully separated. At the same time the supramolecular assemblies are destroyed (dissolved) as shown by DLS. Reasons for this might be a decrease of the concentration of free EGMUDE in solution due to the binding to the gold nanoparticle surface and/or a destabilization of the assemblies by the functionalized nanoparticles itself.

Conclusions

In conclusion, we have shown that EGMUDE not only acts as a stabilizing or protecting agent but also as a reversible flocculator in an aqueous medium. Such a combination does not only provide proof of effective stabilization but also allows the direct concentration of the gold colloid by separation of the sediment. Consequently, we can easily produce gold colloids of up to 0.01 vol%. During the exchange of citrate with EGMUDE the nanoparticles are organized in supramolecular nanoparticle–EGMUDE assemblies, preventing irreversible agglomeration. Furthermore, we demonstrated that the current synthetic protocol is highly valuable to prepare well-dispersed and stable gold colloids.

Acknowledgements

Financial support from the Bundesamt für Berufsbildung und Technologie in the frame of a KTI project (No. P. 8074.1 NMPP-N) is kindly acknowledged.

References

1 D. L. Fedlheim and C. A. Foss, *Metal Nanoparticles: Synthesis, Characterization and Applications*, Marcel Dekker, New York, 2002.
2 Y. Yang, W. Wang, J. Li, J. Mu and H. Rong, *J. Phys. Chem. B*, 2006, **110**, 16867–16873.
3 C. J. Zhong and M. M. Maye, *Adv. Mater*., 2001, **13**, 1507–1511.
4 Y. Kim, R. C. Johnson and J. T. Hupp, *Nano Lett*., 2001, **1**, 165–167.
5 H. Wohltjen and A. W. Snow, *Anal. Chem*., 1998, **70**, 2856–2859.
6 J. F. Hainfeld, *Nature*, 1988, **333**, 281–282.
7 G. Schmid and B. Corain, *Eur. J. Inorg. Chem*., 2003, 3081–3098.
8 J. Kimling, M. Maier, B. Okenve, V. Kotaidis, H. Ballot and A. Plech, *J. Phys. Chem. B*, 2006, **110**, 15700–15707.
9 T. Teranishi, S. Hasegawa, T. Shimizu and M. Miyake, *Adv. Mater*., 2001, **13**, 1699–1701.
10 J. W. Doolittle and P. K. Dutta, *Langmuir*, 2006, **22**, 4825–4831.
11 M. Shena, Y. Dua, N. Huaa and P. Yang, *Powder Technol*., 2006, **162**, 64–72.
12 C.-H. Su, P.-L. Wu and C.-S. Yeh, *J. Phys. Chem. B*, 2003, **107**, 14240–14243.
13 K. Mallicka, Z. L. Wang and T. Pal, *J. Photochem. Photobiol., A*, 2001, **140**, 75–80.
14 N. R. Jana, L. Gearheart and C. J. Murphy, *Langmuir*, 2001, **17**, 6782–6786.
15 G. Frens, *Nature (London) Phys. Sci*., 1973, **241**, 20–22.
16 B. V. Enustun and J. Turkevich, *J. Am. Chem. Soc*., 1963, **85**, 3317–3328.
17 I. E. Sendroiu, S. F. Mertens and D. J. Schiffrin, *Phys. Chem. Chem. Phys*., 2006, **8**, 1430–1436.
18 S. Underwood and P. Mulvaney, *Langmuir*, 1994, **10**, 3427–3430.
19 W. Haiss, N. T. Thanh, J. Aveyard and D. G. Fernig, *Anal. Chem*., 2007, **79**, 4215–4221.
20 P. D. T. Huibers, V. S. Lobanov, A. R. Katritzky, D. O. Shah and M. Karelson, *Langmuir*, 1996, **12**, 1462–1470.
21 J. C. Ravey, A. Gherbi and M. J. Stébé, in *Trends in Colloid and Interface Science II*, Springer, Berlin/Heidelberg, 1988, vol. 76, pp. 234–241.
22 M. J. Rosen, *Surfactants and interfacial phenomena*, Wiley, New York, 1989.
23 P. Becher, *J. Disp. Sci. Technol*., 1984, **5**, 81–96.
24 G. F. Schneider and G. Decher, *Nano Lett*., 2008, **8**, 3598–3604.